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IOP Conf. Series: Materials Science and Engineering **827** (2020) 012034 doi:10.1088/1757-899X/827/1/012034

Enhanced piezoelectric properties of PVdF-HFP/PZT nanocomposite for energy harvesting application

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Abstract. The use of piezoelectric nanocomposite in detection and actuation applications for the development of electromechanical microsystems (MEMS) has become quite common over the last decade. In this paper, we present a flexible piezoelectric nanocomposite films, composed of lead zirconate titanate (PZT) nanoparticles, embedded in poly(vinylidene-difluoride hexafluoro propylene) (PVdF-HFP) matrix. Piezoelectric and ferroelectric properties evolution is proportional to the evolution of the crystalline β-phase. The evaluation of the interactions between PZT and PVdF- HFP, performed by Fourier transform infrared spectroscopy (FTIR), revealed a dramatic improvement in these characteristics over pure PVdF-HFP, and attributed to a better crystallinity of the PVdF-HFP matrix and uniform distribution of nanoparticles. These films nanocomposites were done by solvent casting method, with various concentrations of PZT. Results of these experiments indicate that the investigated thin films nanocomposites are appropriate for various applications in energy storage and energy harvesting application.
Keywords: Energy harvesting; Piezoelectric properties; β-phase; Polyvinylidene difluoride-hexafluoropropylene (PVdF-HFP); Lead zirconate titanate (PZT)

1. Introduction

In recent years, a great deal of research has been done on autonomous energy and in particular on the supply of sensors. Embedded sensors have gained accuracy, reliability, robustness while miniaturizing but they are still limited by the lifespan of their power system [1]. A promising alternative is to recover the ambient mechanical energy to ensure nomadic energy autonomy [2]. At present, these sensors are

powered by batteries that require regular maintenance and pose environmental issues (recycling in particular) [3]. If it is possible to replace these batteries by micro-generators, then the use of this type of sensor will become widespread and will contribute in developing more efficient mechatronic systems. The piezoelectric solution is the most promising because it has the highest electromechanical coupling coefficient, which does not require polarization. Piezoelectric systems are well suited to Microsystem Manufacturing Technologies (MEMS) [4].

A piezoelectric nanocomposite is designed to convert daily human activities and acoustic vibrations into usable electrical energy. When a mechanical energy such as an acoustic wave is applied to the piezoelectric polymer film, electric charges are induced. With this property, a piezoelectric material can be capitalized as an electromechanical energy converter [5].

In this paper, a different tippers of lead zirconate titanate ceramic nanoparticle (PZT) has introduced into the polyvinylidene fluoride-hexafluoropropylene matrix in order to nucleate the crystalline β-phase and eventually improve the piezoelectric properties of the films nanocomposite. This procedure was made by solvent casting-evaporation technique. The characterization of nanocomposite for their structural and morphological analyses are observed by Fourier transform infrared studies and Scanning electron microscopy to confirm the evolution of physicomechanical, thermal, and barrier properties of polymeric nanocomposite for energy storage and energy harvesting application.

2. Experimental section

2.1 Materials

Lead Titanate-Zirconate (PZT) nanoparticles have been used as additives to improve the properties of the PVdF-HFP matrix, was obtained from Sigma Aldrich. The PVdF -HFP (pellets) used has a density of ρ = 1.78 g/cm 3, Mn = 130,000 g/mol and Mw = 400,000 g/mol, was obtained from Sigma Aldrich. N, N-dimethylacetamide (DMAc) is used as the organic polar solvent often used to dissolve hexafluoropropylene polyvinylidene fluoride (PVDF-HFP). It has a density of 0.949 g/cm 3 at 20 °C and a boiling temperature of 163 to 165 °C, was obtained from Sigma Aldrich.

2.2 PVdF-HFP / PZT composite film Preparation

Polyvinylidene fluoride-hexafluoropropylene (PVdF-HFP) was dissolved in N, N-Dimethyl Acetamide (DMAc). In the other hand, different percentages of the nanoparticles of titanate lead zirconate (PZT) are prepared by dispersing the nanoparticles of PZT (powder) in N, N-Dimethyl Acetamide (DMAc). Then, the two solutions are mixed. Afterwards, the mixture is poured and scraped onto a glass plate to enhance the uniformity of the film thickness that will be placed by the glass in an oven at 85 °C for 2 hours, in order to drying the nanocomposite film by evaporation of the solvent.

3. Results and discussions

3.1 Scanning electron microscope (SEM)

Figure 1 shows an SEM image of the Neat PVDF-HFP and its composites of weight of 0.5; 0.8; 1 and 1.5 wt.%, respectively. Figure 1.a shows the PVdF-HFP micrograph. The morphology observed for the copolymer used as a matrix for the composite thus being locked and compressed indicates an indefinite morphology. The PVdF-HFP / PZT micrograph shown in Figure 1.b; 1.c; 1.d; 1.e reveals the homogeneity of the PZT grain distribution. As found in a previous study [6], non-porous composites are only obtained if the ceramic volume fraction is adjusted below about 0.5.

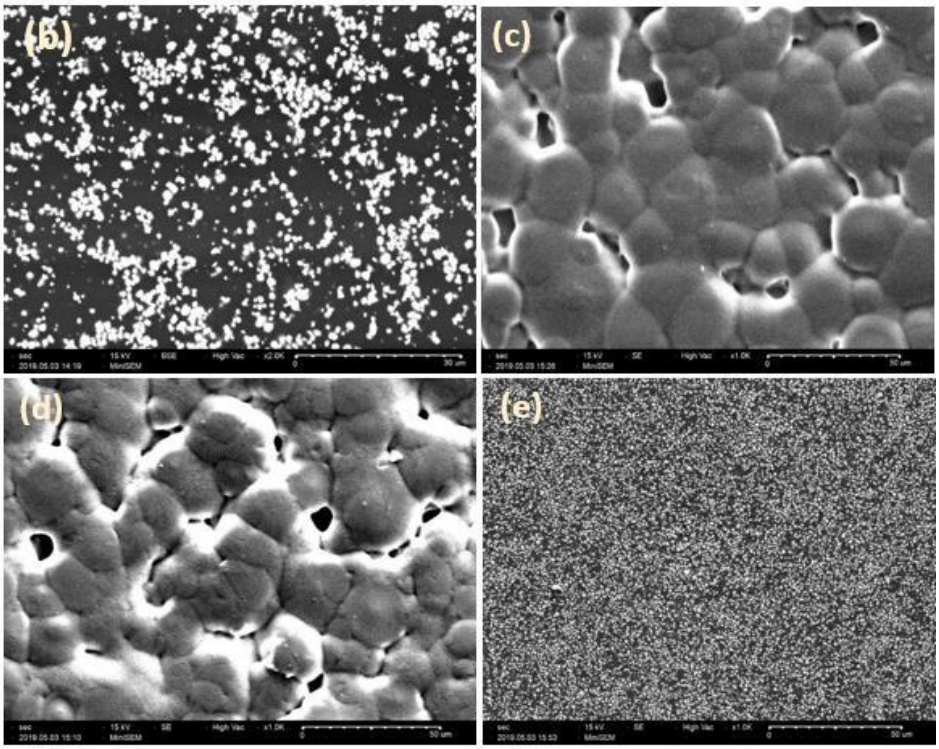

Figure 1. Morphologies of neat PVdF-HFP (a), nanocomposites containing 0.5 wt.% PZT (b), 0.8 wt.% PZT (c), 1 wt.% PZT (d) and 1.5 wt.% PZT under a scanning electron microscope (SEM). PVdF-HFP: polyvinylidene fluoride-co-hexafluropropylene, PZT: Lead zirconate titanate**.**

Therefore, the composite structures shown in Figure 1 represent almost the maximum PZT loading qualities that can be incorporated into PVdF-HFP copolymers while getting autonomous, supple and non-porous films. With higher ceramic weight fractions, brittleness increases considerably and the nanofillers agglomerate and the ceramic particles are not completely covered by the polymer which leads to a porous structure [7-8].

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The crystallinity of PVdF-HFP/PZT nanocomposites were further analyzed by FTIR spectra and represented in Figure 2. The vibrational peaks observed at 1071, 1176, 1397 cm^{-1} were due to bending vibration C – C, swinging vibration CH_2, motion vibration CF_2 group in neat PVdF-HFP respectively [9]. The vibrational peaks observed at 796 and 1071 cm^{-1} were due to the non-polar crystalline α-phase of PVdF-HFP [10]. The absence of a band corresponding to the bending of OH confirms that the neat PVdF-HFP and composite PVdF-HFP-PZT films are hydrophobic in nature. This is noticed from the addition of a fraction of 0.1 wt. % of PZT nanofillers up to 1.5 wt.%.

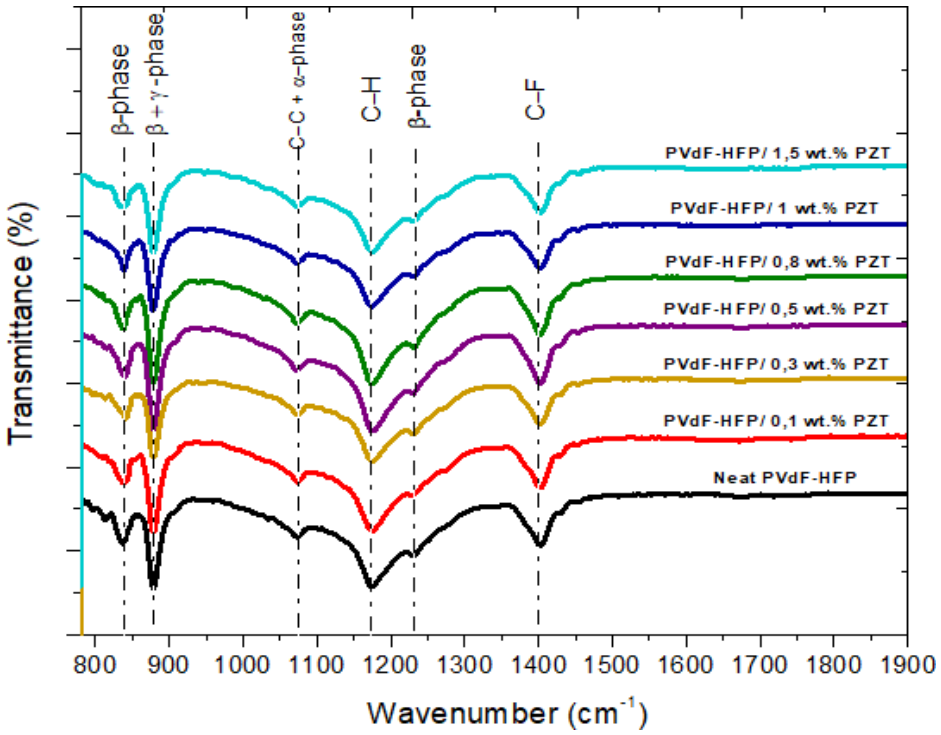

Figure 2. FTIR spectra of PVDF-HFP and PVDF-HFP / PZT nanocomposites containing 0.1, 0.3, 0.5, 0.8, 1, and 1.5 wt. % PZT, respectively. FTIR: Fourier transform infrared spectroscopy; PVdF-HFP: poly (vinylidene fluoride-co-Hexafluoride propylene); PZT: Lead zirconate titanate.

The nucleation of the fully polar β-phase in the PVdF-HFP/PZT composites film were clearly shown from the appearance of the intense vibrational band at 1232 cm^{-1}, which is not present in the Neat PVdF-HFP film (Figure 1). The semi polar γ-phase is present in both the Neat PVdF-HFP and the PVdF-HFP/PZT composite films as observed from the 1176 cm^{-1} peak. However, it gets reduced because of the β-phase nucleation in the composite film. The dual character peaks (β and γ-phases) at 882 cm^{-1} also indicate the β-phase formation in the PVdF-HFP/PZT composites film.

4. Conclusion

In order to evaluate the physicomechanical, morphological, and barrier properties of polymeric nanocomposites for energy harvesting, PZT was mixed with PVDF-HFP in a specific ratio following the simple method of solvent casting-evaporation. The composites obtained showed a good piezoelectric response, which has been demonstrated in terms of crystallinity derived from FTIR analysis. The FTIR analysis shows the interaction between PZT and PVdF-HFP, where the α-crystal content decreases while the β-crystal content increases. Indeed, the formation of the β-phase was well observed in these nanocomposites showing the efficiency of the functionalization of titanate lead zirconate (PZT) nanofillers on the PVdF-HFP matrix.

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